Methyl bromide emissions to the atmosphere from temperate woodland ecosystems

Cite As: Drewer, J, Heal, KV, Smith, KA & Heal, MR 2008, 'Methyl bromide emissions to the atmosphere from temperate woodland ecosystems' *Global Change Biology*, vol 14, no. 11, pp. 2539-2547.

DOI: 10.1111/j.1365-2486.2008.01676.x

Methyl bromide emissions to the atmosphere from temperate woodland ecosystems

Authors: Julia Drewer, Kate V. Heal, Keith A. Smith and Mathew R. Heal

Address for correspondence:

Dr. M R Heal
School of Chemistry
University of Edinburgh,
Joseph Black Building,
West Mains Road,
Edinburgh, UK
EH9 3JJ

m.heal@ed.ac.uk

Methyl bromide fluxes in temperate woodland ecosystems – a previously unrecognised net source

Julia Drewer[1,2,*], Kate V. Heal[2], Keith A. Smith[2] and Mathew R. Heal[1]

[1]School of Chemistry, The University of Edinburgh, Joseph Black Building, West Mains Road, Edinburgh, EH9 3JJ, UK.

[2]School of GeoSciences, The University of Edinburgh, Crew Building, West Mains Road, Edinburgh, EH9 3JN, UK.

* current address: Centre for Ecology & Hydrology, Edinburgh Research Station, Bush Estate, Penicuik, Midlothian, EH26 0QB, UK.

Author for correspondence:

Dr. M. R. Heal, School of Chemistry, The University of Edinburgh, Joseph Black Building, West Mains Road, Edinburgh, EH9 3JJ, UK.

Tel: +44 (0)131 6504764

Fax: +44 (0)131 6506543

m.heal@ed.ac.uk

Keywords:

emissions, enclosure, CH3Br, flux, litter, ozone layer, Scotland, woodland.

Running title (43 characters including spaces):

Methyl bromide fluxes in temperate woodland

Abstract

The environmental importance of methyl bromide (CH_3Br) arises from its contribution to stratospheric ozone loss processes and, as a consequence, its emissions from anthropogenic sources are subject to the Montreal Protocol. A better understanding of the natural budget of CH_3Br is required for assessing the benefit of anthropogenic emission reductions and for understanding any potential effects of environmental change on global CH_3Br concentrations. Measurements of CH_3Br flux in temperate woodland ecosystems, in particular, are very sparse, yet these cover a large fraction of terrestrial land surface. Results presented here from 18 months of field measurements of CH_3Br fluxes in four static flux chambers in a woodland in Scotland and from enclosures of rotting wood and deciduous and coniferous leaf litter suggest that emissions from temperate woodlands have been underestimated. Net CH_3Br fluxes in the woodland varied between the chambers, fluctuating between net uptake and net emissions (-73 to 279 ng m^{-2} h^{-1} across 161 individual measurements), and with no strong seasonality, but with time-averaged net emission overall (27 ng m^{-2} h^{-1}). This work demonstrates that scale-up needs to be based on sufficient individual measurements to provide a reasonably-constrained estimate of the long-term mean. Mean (range) net CH_3Br fluxes from deciduous and coniferous leaf litter were 43 (17 to 33) ng kg^{-1} (dry weight) h^{-1} and 80 (19-137) ng kg^{-1} (dry weight) h^{-1}, respectively, and ~1-2 ng kg^{-1} (fresh weight) h^{-1} from rotting deciduous woody litter. A direct multiplicative scale-up of these flux data yields the values of ~3, ~12 and ~2 Gg y^{-1} for global CH_3Br source from temperate woodland soil, fine litter and coarse litter, respectively, subject to unquantified uncertainty. Despite the intrinsic variability, the data obtained here consistently point to an average net emission flux and to the conclusion that the temperate forest soil/litter ecosystem is a previously unrecognised net source of CH_3Br.

Introduction

Methyl bromide (CH_3Br) is a trace gas emitted to the troposphere from various sources. Its lifetime in the atmosphere is sufficiently long (current best estimate 0.7 y (WMO, 2007)) that a significant proportion can reach the stratosphere, where, via the Br radical released by photolysis, it is a major contributor to stratospheric ozone loss processes. Since it is estimated that CH_3Br contributes ~37% of all Br reaching the stratosphere (WMO, 2007), anthropogenic sources of CH_3Br are being phased out under the Montreal protocol. However, anthropogenic sources of CH_3Br are small compared with its natural fluxes from terrestrial and marine ecosystems. The latter are estimated to contribute ~80% of the CH_3Br reaching the stratosphere, but there is considerable uncertainty in quantifying the natural fluxes because of the paucity of data on process mechanisms and extent of variability. The most authoritative evaluation of the global budget for CH_3Br, published by the WMO Global Ozone Research and Monitoring Project, reports a total sink flux (204 Gg y^{-1}) that exceeds the total source flux (159 Gg y^{-1}) by approximately one-quarter (WMO, 2003), but with enormous ranges of uncertainty in each estimate (129-387 Gg y^{-1} and 77-293 Gg y^{-1}, respectively). The most recent WMO assessment (WMO, 2007) does not report any quantified progress towards resolution of the CH_3Br source/sink discrepancy. Modelling studies have suggested the imbalance cannot be explained by the large range of uncertainty (Reeves, 2003) but is due to unidentified natural sources rather than to sink terms that have been overestimated (Saltzman *et al.*, 2004; Warwick *et al.*, 2006).

Although natural processes might initially appear to be an issue over which humankind has little or no control, the lack of CH_3Br budget closure is important for a number of reasons.

First, global atmospheric chemistry models require quantitative data on all CH_3Br sources/sinks for accurate prediction of the trajectory of stratospheric ozone levels. Secondly, many natural CH_3Br sources/sinks are directly and indirectly influenced by human activity, most notably via changes in land cover and management and via future regional climate changes likely to be induced by anthropogenic radiative forcings. In addition, as anthropogenic phase-out of CH_3Br continues, the magnitudes of natural fluxes of CH_3Br become relatively more important.

The consensus is that the CH_3Br budget lacks adequate identification and quantification of terrestrial sources. Temperate woodlands cover an estimated 12.9×10^6 km^2 around the globe (Matthews, 1983) but there have been very few measurements of ambient fluxes within this ecosystem. Shorter *et al.* (1995) and Serça *et al.* (1998) conducted in-situ CH_3Br uptake experiments over forest soils using enclosures into which CH_3Br was injected. Both studies reported rapid CH_3Br uptake, from which they estimated global sink fluxes for CH_3Br in temperate forest soils of 22 Gg y^{-1} and 38 ± 30 Gg y^{-1}, respectively. However, these enclosure studies used initial CH_3Br mixing ratios 2-3 orders of magnitude greater than ambient (600 pptv and 5 ppbv, respectively) and do not address the issue of net flux from forest soil under unperturbed, ambient conditions. To our knowledge only two published studies do. Dimmer *et al.* (2001) reported median net CH_3Br emission equivalent to 17×10^{-4} g m^{-2} y^{-1} (range 3 – 65×10^{-4} g m^{-2} y^{-1}) from two enclosures on peaty soils under conifer plantation in Galway, Ireland, for n = 14 measurements in September, whilst Varner *et al.* (2003) reported mean net CH_3Br uptake equivalent to 0.70 μg m^{-2} d^{-1} (range from 4.0 μg m^{-2} d^{-1} net uptake to 3.0 μg m^{-2} d^{-1} net emission) from two enclosures in mixed deciduous conifer woodland in New Hampshire, USA, for n = 28 measurements between May and September. In comparable units, the median net emission flux of Dimmer *et al.* (2001) corresponds to 4.6 μg m^{-2} d^{-1}, and

is therefore not only in a different direction to the mean net uptake flux of Varner *et al.* (2003) but of substantially greater magnitude. Additional laboratory experiments led Varner *et al.* (2003) to conclude that the measured woodland CH_3Br fluxes were the net outcome of consumption and production processes occurring at the same time and that the net flux may be a relatively small difference compared with the separate consumption and production fluxes.

One specific likely source of CH_3Br in woodland ecosystems is fungal activity, in particular the Hymenochaetaceous genera ("white rot" fungi), acting on woody and non-woody litter on the forest floor. Although most research on these fungi has focused on CH_3Cl production (Harper *et al.*, 1988; Harper and Hamilton, 1988; Harper, 1998) it has also been shown that Br is preferentially methylated over Cl (Harper, 1985; Harper and Kennedy, 1986). Lee-Taylor and Holland (2000) combined the halide methylating efficiencies measured by Harper and co-workers with estimates of annual litter decomposition rates and bromide content to estimate global annual CH_3Br source fluxes of 1.7 (0.5 – 5.2) Gg y^{-1}, ~4 Gg y^{-1} and ~5 Gg y^{-1} from above-ground woody litter decay, above-ground fine litter decay and below-ground wood/litter decay, respectively. The above are laboratory and modelling studies, although Moore *et al.* (2005) reported CH_3Cl emissions from enclosures of rotting wood in a tropical forest (CH_3Br fluxes were not measured). There is also evidence that ectomycorrhizal fungi, which are common in woodland (associated with tree roots), may be an important source of methyl halides to the atmosphere (Redeker *et al.*, 2004).

Overall there is clearly limited and conflicting evidence from laboratory and field measurements to date as to whether temperate woodland ecosystems are a net source or sink of CH_3Br. Since the global area of temperate woodlands is very large, CH_3Br fluxes from this ecosystem have potential to contribute significantly to the global CH_3Br budget. In this

research, long-term measurements of CH_3Br net flux from four field enclosure chambers in a temperate woodland in Scotland were made from March 2005 to August 2006, providing a dataset of 161 individual measurements, substantially larger than previous studies. Relationships between net fluxes and environmental variables such as air and soil temperature and methane net flux were examined to explore processes influencing CH_3Br emissions. Rotting wood, deciduous leaf and coniferous needle litter were also investigated to determine potential net fluxes of CH_3Br from these substrates.

Materials and Methods

Field measurements

Four collars (internal diameter 24 cm) for enclosure chambers made of opaque hard plastic (PVC) and with a headspace volume of 0.0058 m^3 were set up permanently in the Hermitage of Braid woodland (55°55′ N, 3°12′ W), a local nature reserve of 53 ha in southern Edinburgh, Scotland. The semi-natural woodland dates from the early 19th century and is dominated by beech (*Fagus sylvatica*), ash (*Fraxinus excelsior*) and sycamore (*Acer pseudoplatanus*). The collars were arranged as replicate pairs about 3 m apart within two contrasting areas of vegetation in the woodland. Collars I1 and I2 were placed in ivy (*Hedera helix*) covered ground beneath trees at the top of a slope, and collars B3 and B4 were placed in a beech dominated area underlain by leaf litter. Occasionally small plants such as willowherb (*Epilobium* spec.) or bramble (*Rubus fruticosus*) grew inside the collars for a few weeks. There were no distinctive differences in soil properties between the two areas. The soil was a sandy loam with a mean pH of 5.5 (n = 4) and a mean organic matter content in the top 10 cm, derived by loss after ignition at 500 °C, of 10% w/w oven-dry soil (n = 4). Water-extractable soil Br^- content was below the detection limit of 1.4 μg Br^- g^{-1} dry weight soil.

Enclosure lids were used only for the 10 min duration of enclosure so as not to influence vegetation and soil within the collars. At the end of the enclosure, a 400 mL air sample from the headspace was extracted into a 1000 mL gas-tight syringe via a tap in the centre of the lid and transferred to a pre-evacuated 1 L Tedlar bag. Sample bags were stored in the dark at room temperature until analysis on the same day or within 24 h. Experiments showed no loss of CH_3Br under these storage conditions. On each sampling occasion measurements were also made of the air and 10 cm soil temperatures. Samples were taken every one to two weeks from March 2005 until August 2006.

Samples of deciduous leaf litter, primarily of *Acer pseudoplatanus* (sycamore) were collected from the woodland floor near the enclosure collars on five occasions between November and December 2005, and on four occasions between November 2006 and January 2007. A substantial proportion of leaf litter was noted to be infected with the *Rhytisma* fungus. As soon as possible after collection, between 2 and 8 sub-samples of each bulk sample were enclosed separately in an opaque plastic container of 10 L volume and headspace air withdrawn after a fixed time interval through a three-way tap in the lid. Enclosures of the container only showed no measurable CH_3Br flux. Net fluxes were also measured in the same manner from samples of needle litter of *Picea sitchensis* (Sitka spruce) and *Pinus sylvestris* (Scots pine) collected at intervals during 2006 from nearby conifer forests. Three samples of rotting beech wood were also collected from the deciduous woodland floor.

Analysis

The CH_3Br was quantified using an HP 5890 gas chromatograph equipped with an electron capture detector and a DB624 capillary column (J&W Scientific, 30 m long, 0.32 mm i.d., 1.8

µm film). The temperature programme was 40 ºC for 5 min, ramping at 40 ºC min^{-1} to 240 ºC and hold for 5 min. 10% methane in argon was used for both the carrier gas (flow 1.3 mL min^{-1}) and the make-up gas for the ECD (flow 25 mL min^{-1}). A two-trap pre-concentration unit was used prior to GC separation in order to quantify CH_3Br concentrations to lower than 10 pptv (Drewer *et al.*, 2006). The first trap comprised a 1/4-inch stainless steel tube filled with 0.59 g of Tenax, which was Peltier-cooled to -4 °C during sample loading to enhance the efficiency of adsorption. The sample was then transferred by heating to the second trap, which consisted of 20 cm of 1/8-inch stainless steel tubing filled with fine glass beads and cooled to -79 °C using dry ice. Calibration standards in the range 10–1000 pptv were prepared volumetrically in air using a certified 500 ppbv CH_3Br standard in nitrogen (Air Products Inc.). The average analytical relative error in CH_3Br quantification was evaluated to be ±15%. The detection limit for quantification of net flux was determined by the ability to discriminate a significant difference in CH_3Br concentration between a headspace sample from an enclosure and a contemporaneous sample of ambient air. From the variability of replicates and uncertainty in calibration fits it was estimated that a significant difference in mixing ratio was 4 pptv, corresponding to a field chamber net CH_3Br flux of 12 ng m^{-2} h^{-1}. Limits of detection for net fluxes from the deciduous and coniferous litter enclosures were determined to be 24 and 10 ng kg^{-1} (dry weight) h^{-1}, respectively.

Some enclosure headspace samples were also analysed for methane (CH_4) using a separate HP 5890 gas chromatograph equipped with a flame ionisation detector (GC-FID). Separation was on a 1/8-inch packed column (Poropak QS 80-100 mesh) at 50 °C with injector and detector temperatures of 70 °C and 250 °C, respectively. Gas flow rates were 21 mL min^{-1} for the nitrogen carrier, and 25 and 63 mL min^{-1}, respectively, for the hydrogen and air for the

FID. The Tedlar bags containing the gas samples were connected via luer fittings to an automated injection system fitted to the GC.

Statistical analysis of data was conducted using Minitab 15 software and a significance level of $p < 0.05$.

Results and Discussion

Time series of woodland soil net flux

The net CH_3Br flux from the woodland chambers fluctuated between positive (emission) and negative (uptake) (Figure 1a). A summary of fluxes from each chamber separately and combined over the whole measurement period is shown in Table 1. The mean measured net flux from the chambers varied between 17 and 33 ng m^{-2} h^{-1}, with an overall mean of all measured fluxes of 27 ng m^{-2} h^{-1}. The median measured net flux from the chambers varied between 5 and 18 ng m^{-2} h^{-1}, with an overall median of all measured fluxes of 8 ng m^{-2} h^{-1}. There was no significant statistical difference (MANOVA) in flux with time between the two types of woodland location (chambers I and chambers B). In general, the net fluxes from the four chambers exhibited the same variation between one measurement occasion and another, but superimposed on this were clear instances of periodic excursions of considerably higher emissions from a particular chamber at particular times. There was no discernible pattern to these excursions, or relationship to other measured or observable features at the monitoring locations, except that the prolonged period of net emissions from chamber B3 between July and September 2005, when all the other chambers exhibited zero or small uptake flux, coincided with the growth of an *Epilobium* spec. (willowherb) within the collar.

Even though fluxes fluctuated between net uptake and net emission, the mean/median net flux over the whole measurement period was emission. Re-calculating mean fluxes using zero for all fluxes smaller than the net flux detection limit of |12| ng m^{-2} h^{-1} did not change the mean net emission values shown in Table 1 by more than ±2 ng m^{-2} h^{-1}.

There was no apparent seasonal pattern in fluxes from these chambers (although see later for discussion of fluxes in relation to temperature). Overall mean fluxes were similar in winter (25 ng m^{-2} h^{-1}, October to February) and summer (28 ng m^{-2} h^{-1} March to September). Overall median flux in winter (0 ng m^{-2} h^{-1}) was lower than the median flux of 18 ng m^{-2} h^{-1} for the two summer periods, but the means were similar because of the predominance of the short-term excursions of higher emissions in winter.

From May 2005 to June 2006 air samples from the woodland chamber enclosures were also analysed for CH_4 in order to investigate whether there was any relationship between CH_4 and CH_3Br net fluxes (Figure 1b). Net CH_4 fluxes were three orders of magnitude greater than net CH_3Br fluxes and were mainly negative, with uptake generally a few tens of μg m^{-2} h^{-1}, but increasing to about 150 μg m^{-2} h^{-1} in autumn. The time series of net CH_4 fluxes were generally similar for all four chambers. On the few occasions on which net emissions of CH_4 were measured, soil conditions were very wet and thus presumed anaerobic. Mean measured net CH_4 fluxes for individual chambers ranged between -30 and -40 μg m^{-2} h^{-1}, with an overall mean net flux of -34 μg m^{-2} h^{-1}. Median measured net CH_4 fluxes for individual chambers ranged between -17 and -28 μg m^{-2} h^{-1}, with an overall mean net flux of -21 μg m^{-2} h^{-1}. Thus, overall, there was net uptake of CH_4 for the year of measurements. Methane fluxes measured at this woodland site were within the range for seven UK woodland sites of -135 to +45 μg m^{-2} h^{-1} reported by Smith *et al.* (2000). A pairwise scatter plot (not shown) of the data in Figures

1a and 1b showed there was no quantitative relationship between measured CH_3Br and CH_4 fluxes. This suggests that different processes are involved in CH_4 and CH_3Br production and uptake.

There were no strong relationships between CH_3Br fluxes from the individual chambers and soil and air temperature (which were closely coupled because of the canopy shading). There was a slight trend for greater net CH_3Br emissions from chambers I1 and I2 at cooler temperatures and for higher emissions from chamber B3 to be associated with warmer temperatures (Figure 2). This could be due to less uptake in chambers I1 and I2 during cooler conditions, whereas in chamber B3 higher emissions could be associated with production from rotting of leaf litter in moderate temperatures.

Diurnal measurements of CH_3Br fluxes were made at each enclosure on one day in summer and one day in winter, as shown in Figure 3. The associated soil and air temperatures varied only slightly during the days on which flux measurements were carried out, remaining in the ranges 14-15 ºC and 14-18 ºC, respectively, for the summer measurements and the ranges 5-6 ºC and 4-7 ºC, respectively, for the winter measurements.

Net CH_3Br flux from enclosure B3 in the summer diurnal measurement series showed the same high emissions that were observed in the series of regular weekly or two-weekly measurements being made around this time (Fig. 1) and were attributed to the growth of a willowherb plant within the enclosure. The net emission from this enclosure peaked around midday, and was therefore consistent with an association with a solar cycle as reported for CH_3Br emissions from a nearby vegetated salt marsh (Drewer *et al.*, 2006). The diurnal fluxes from the other three enclosures were close to zero, also consistent with the regular time series

measurements from these chambers around this time. Although small and close to, or below, the formal limit of detection, these fluxes also exhibited a tendency to be positive, or less negative, during the middle of the day.

Fluxes during the winter diurnal measurements were uptake or close to zero, but again with a slight tendency to be less negative during the middle of the day.

Fluxes from woody and non-woody litter

Mean net CH_3Br fluxes from the sub-samples of deciduous and coniferous litter collected on each sampling occasion are shown in Figures 4 and 5, respectively. The mean (median) net flux from the coniferous needle litter of 80 (86) ng kg^{-1} (dry weight) h^{-1} (n = 7 sampling occasions) was approximately double the mean (median) net flux from the deciduous leaf litter of 43 (40) ng kg^{-1} (dry weight) h^{-1} (n = 9 sampling occasions). The magnitudes of the standard errors plotted in Figures 4 and 5 show there was frequently a wide variation in the measured fluxes between the sub-samples of a single bulk sample. Despite this heterogeneity, net CH_3Br fluxes from litter were persistently positive (emission) overall, with fluxes from the deciduous leaf litter showing a persistent decline throughout the late autumn and winter in both years of sampling, presumably related to changing rates of litter decay. Fluxes from the coniferous needle litter did not show seasonal variation exceeding the within-sample variation of sub-sample replicates. Overall, these data show that decaying temperate deciduous and coniferous litter are both net sources of CH_3Br that need to be considered in a global budget.

Net CH_3Br fluxes from sub-samples of the three samples of rotting beech wood were low. Although an emission of 16 ng kg^{-1} (fresh weight) h^{-1} was measured on one occasion, other measured net fluxes were close to or below the limit of detection, calculated to be equivalent

to 1.6 ng kg^{-1} (fresh weight) h^{-1} net flux for these measurements. In a further experiment, two sub-samples with visible fungi from the same rotting log were enclosed on four occasions over three days at laboratory temperature and the visible fungi material then removed and the fluxes re-measured for a further two days. Even though some of the measured fluxes were below the calculated detection limit, lower or negative emissions tended to occur after the fungi were removed.

Global scale-up of observed CH_3Br fluxes from temperate woodland

Table 2 compares the data for CH_3Br fluxes obtained from the woodland matrices studied here with the few data reported previously in the literature. The current study comprises a considerably higher number of individual measurements, and over a much longer time period, than previous studies. Of the two previous studies measuring ambient flux in a woodland, one derives a net uptake overall for CH_3Br (Varner *et al.*, 2003) and one a net emission (Dimmer *et al.*, 2001). However, as with the current study, both these previous studies report a wide range in fluxes (both uptake and emission) from individual measurements.

The data collected in this work were crudely scaled-up to global values as follows. The overall mean flux during the 18 months of regular measurement at the four below-canopy sites monitored in this work was 27 ng m^{-2} h^{-1}. In the absence of any clearly discernible seasonal or diurnal trend in the measurements it is reasonable to take the overall mean as the best estimate for annual average net flux at this woodland. This yields an annual CH_3Br emission of 240 μg m^{-2}. Applying a global area of temperate forest of 12.9×10^{12} m^2 (Matthews, 1983) yields an estimated global CH_3Br flux of 3.1 Gg y^{-1} from this source. The lowest and highest of the mean fluxes from the four chambers at this site equate to global CH_3Br fluxes of 1.9 and 3.7 Gg y^{-1}. Even though the fluxes from the individual chambers

were quite small, about an order of magnitude lower than those from a nearby salt marsh (Drewer *et al.*, 2006), they result in a considerable global annual flux because of the large area of temperate woodlands. This global emission flux of ~3 Gg y^{-1} for temperate woodlands has not previously been included in global budgets of CH_3Br.

Estimates of global woodland litter production are summarised by Lee-Taylor and Holland (2000), and have values of ~25 Pg (dry weight) y^{-1} for non-woody litter and ~22 Pg (dry weight) y^{-1} for the sum of above-ground coarse and fine woody litter. To convert these annual production rates into global mass of these two categories of litter requires assumption of their respective average turnover times. An assumption of one and two year average turnover times for non-woody litter and woody detritus yields estimates for masses of these materials globally of ~25 Pg (dry weight) and ~50 Pg (dry weight), respectively. In this work, the mean (range) net CH_3Br emissions from sub-samples of deciduous and coniferous non-woody litter collected on a number of occasions were 43 (17-33) and 80 (19-137) ng kg^{-1}(dry weight) h^{-1}, respectively. Making the further arbitrary assumption that global non-woody litter comprises two-thirds deciduous and one-third coniferous material, gives an estimated total global flux of CH_3Br from non-woody litter of 6 (2.5-4.8) (deciduous) + 6 (1.4-10) (coniferous) = 12 (4-15) Gg y^{-1}. Likewise, combining the mean net CH_3Br emission of 2 ng kg^{-1} (fresh weight) h^{-1} obtained here for rotting woody detritus with the above-estimated global mass of 50 Pg (and taking a 1:1 dry:fresh weight ratio) gives a global flux from this source of 2 Gg y^{-1}.

Clearly the uncertainties and assumptions in the data contributing to these global estimates are so many that it is not possible to derive a reliable quantitative confidence interval on the central value; the estimates represent “order of magnitude” only. However, it is useful to note the assumptions to which the global estimates are more or less sensitive. The largest

uncertainty is, of course, in the extrapolation of mean net flux values obtained in this work to all such material globally. The data presented here for in-situ emissions of CH_3Br from leaf litter are, to the best of the authors' knowledge, the only such data available. Whilst higher rates of CH_3Br emission might be expected at the higher temperatures in the tropics, this will presumably be offset by the faster turnover time of litter in the tropics. Nevertheless, changing the assumed global split between deciduous and coniferous non-woody litter, and/or the assumed average turnover times of the litter (within reasonable values) does not alter the global estimates by more than a factor of ~3 up or down, i.e. an uncertainty contained within an order of magnitude variation.

The estimates obtained here of ~2 Gg y^{-1} and 4-15 Gg y^{-1} for emissions of CH_3Br from woody and non-woody above-ground litter can be compared with the only previous estimates for these fluxes, of 1.7 (0.5-5.2) Gg y^{-1} and ~4 Gg y^{-1} respectively, reported by Lee-Taylor and Holland (2000) from model simulations using laboratory data on wood-rotting fungi (Table 2). Given the different methodological approaches, and the inevitable large uncertainties inherent in the extrapolations in both methods, the two sets of estimates compare well in indicating net emission of CH_3Br from woodland media.

Conclusions

The CH_3Br fluxes from deciduous woodland soil, rotting wood and deciduous and coniferous litter reported here represent the most detailed dataset for temperate woodlands. An overall net positive flux (i.e. emission) of CH_3Br from temperate deciduous forest floor (and deciduous and coniferous above-ground litter) has been demonstrated in this work. This is in contrast to some previous literature reports of net uptake of CH_3Br by temperate forest soil

and implies that total temperate woodland emissions of CH_3Br are probably currently underestimated. This conclusion is founded on measurements conducted regularly over a period of more than 18 months. Although net flux from a specific forest location or specific forest material is inevitably subject to considerable spatial and temporal variability, the long-term mean fluxes are reasonably consistent with each other to within an order of magnitude. Although any attempt at extrapolating site-specific measurements to global scale is clearly subject to large uncertainty, these data nevertheless suggest that temperate forest soil/litter ecosystems may contribute significantly to the global net source of CH_3Br and at least as much as salt marshes globally.

Acknowledgements

Funding for this work and for JD was provided by The University of Edinburgh and the UK EPSRC. Permission from the City of Edinburgh Council to undertake fieldwork at the woodland in the Hermitage of Braid is gratefully acknowledged as is the assistance of Jacqueline Ross and Helena Woodvine in the collection and analysis of some of the litter data.

References

Dimmer CH, Simmonds PG, Nickless G, Bassford MR (2001) Biogenic fluxes of halomethanes from Irish peatland ecosystems. *Atmospheric Environment*, **35**, 321-330.

Drewer J, Heal MR, Heal KV, Smith KA (2006) Temporal and spatial variation in methyl bromide emissions from a salt marsh. *Geophysical Research Letters*, **33**, L16808, doi:10.1029/2006GL026814.

Harper DB (1985) Halomethane from halide ion - a highly efficient fungal conversion of environmental significance. *Nature*, **315**, 55-57.

Harper DB (1998) Biosynthesis and utilization of chloromethane by fungi. *Journal of Chemical Technology and Biotechnology*, **71**, 366-367.

Harper DB, Hamilton JTG (1988) Biosynthesis of chloromethane in Phellinus-Pomaceus. *Journal of General Microbiology*, **134**, 2831-2839.

Harper DB, Kennedy JT (1986) Effect of growth conditions on halomethane production by Phellinus species - biological and environmental implications. *Journal of General Microbiology*, **132**, 1231-1246.

Harper DB, Kennedy JT, Hamilton JTG (1988) Chloromethane biosynthesis in Poroid fungi. *Phytochemistry*, **27**, 3147-3153.

Lee-Taylor JM, Holland EA (2000) Litter decomposition as a potential natural source of methyl bromide. *Journal of Geophysical Research-Atmospheres*, **105**, 8857-8864.

Matthews E (1983) Global vegetation and land-use - new high-resolution data-bases for climate studies. *Journal of Climate and Applied Meteorology*, **22**, 474-487.

Moore RM, Gut A, Andreae MO (2005) A pilot study of methyl chloride emissions from tropical woodrot fungi. *Chemosphere*, **58**, 221-225.

Redeker KR, Treseder KK, Allen MF (2004) Ectomycorrhizal fungi: A new source of atmospheric methyl halides? *Global Change Biology*, **10**, 1009-1016.

Reeves CE (2003) Atmospheric budget implications of the temporal and spatial trends in methyl bromide concentration. *Journal of Geophysical Research-Atmospheres*, **108**, 4343, doi:10.1029/2002JD002943.

Saltzman ES, Aydin M, De Bruyn WJ, King DB, Yvon-Lewis SA (2004) Methyl bromide in preindustrial air: Measurements from an Antarctic ice core. *Journal of Geophysical Research-Atmospheres*, **109**.

Serca D, Guenther A, Klinger L, Helmig D, Hereid D, Zimmerman P (1998) Methyl bromide deposition to soils. *Atmospheric Environment*, **32**, 1581-1586.

Shorter JH, Kolb CE, Crill PM, Kerwin RA, Talbot RW, Hines ME, Harriss RC (1995) Rapid degradation of atmospheric methyl-bromide in soils. *Nature*, **377**, 717-719.

Smith KA, Dobbie KE, Ball BC, et al. (2000) Oxidation of atmospheric methane in Northern European soils, comparison with other ecosystems, and uncertainties in the global terrestrial sink. *Global Change Biology*, **6**, 791-803.

Varner RK, White ML, Mosedale CH, Crill PM (2003) Production of methyl bromide in a temperate forest soil. *Geophysical Research Letters*, **30**, 1521, doi:10.1029/2002GL016592.

Warwick NJ, Pyle JA, Shallcross DE (2006) Global modelling of the atmospheric methyl bromide budget. *Journal of Atmospheric Chemistry*, **54**, 133-159.

WMO, (2003) Scientific assessment of ozone depletion: 2002. Global Ozone Research and Monitoring Project Report No. 47., World Meteorological Organization, Geneva.

WMO, (2007) Scientific assessment of ozone depletion: 2006. Global Ozone Research and Monitoring Project Report No. 50., World Meteorological Organization, Geneva.

Tables

Table 1: Summary of CH_3Br net fluxes measured from four woodland enclosures between March 2005 and August 2006.

	Net flux of CH_3Br / ng m^{-2} h^{-1}				
chamber	**I1**	**I2**	**B3**	**B4**	**all**
n	39	42	39	41	161
mean	33	25	33	17	27
median	1	5	18	8	8
min	-30	-29	-73	-71	-73
max	279	244	263	93	279

Table 2: Summary of data from this work and reported in the literature of net fluxes of CH_3Br from woodland ecosystems.

Reference	Location	Type of study	CH_3Br flux determination	Number of measurements
Shorter *et al.* (1995)	Durham, New Hampshire, USA (43°08′N, 71°57′W)	CH_3Br-dosed field enclosures at a mixed deciduous and conifer forest	-22 Gg y^{-1} global temperate woodland	Not given
Serça *et al.* (1998)	Denver, Colorado, USA	CH_3Br-dosed field enclosures at a cottonwood and deciduous shrub site	-38 ± 30 Gg y^{-1} global temperate woodland	Not given
Lee-Taylor and Holland (2000)	---	Modelling study using estimates for litter decay, bromide content and fungal CH_3Br production	+1.7 (0.5-5.2) Gg y^{-1} global above-ground woody litter ~ +4 Gg y^{-1} global above-ground fine litter	---
Dimmer *et al.* (2001)	Galway, Ireland (53°19′N, 9°54′W)	Ambient field enclosures at two conifer plantations on peat	+190 (+3 to +740) ng m^{-2} h^{-1} [a] (no global estimate provided)	14
Varner *et al.* (2003)	Durham, New Hampshire, USA (43°08′N, 71°57′W)	Ambient field enclosures at a mixed deciduous and conifer forest	-30 (-120 to +170) ng m^{-2} h^{-1} [b] -2.2 ± 0.9 Gg y^{-1} global temperate woodland	28
This work	Edinburgh, Scotland, UK 55°55′N, 3°12′W	Ambient field enclosures at a deciduous wood on sandy loam	+27 (+17 to +33) ng m^{-2} h^{-1} [c]	161
		deciduous leaf litter	+43 (+8 to +98) ng kg^{-1} dwt h^{-1} [d]	35
		coniferous needle litter	+80 (+19 to +137) ng kg^{-1} dwt h^{-1} [d]	19
		rotting wood	+1.6 ng kg^{-1} fwt h^{-1}	10

[a] Converted from authors' reported units of g m^{-2} y^{-1}.
[b] Converted from authors' reported units of µg m^{-2} d^{-1}.
[c] Quoted range is min and max of the mean flux from 4 enclosures March 2005 to August 2006.
[d] Quoted range is min and max of the mean flux of sub-sample replicates.

Figure legends

Figure 1: Net fluxes of (a) CH_3Br and (b) CH_4 at four locations in deciduous woodland measured between March 2005 and August 2006. Data for B3 cease in mid-June 2006 when the chamber disappeared, presumed stolen. The limit of detection of net CH_3Br flux was calculated to be ±12 ng m^{-2} h^{-1}. The solid line in (a) shows the 10 cm depth soil temperature.

Figure 2: Net CH_3Br flux as a function of 10 cm depth soil temperature at time of sampling for the four woodland chambers throughout the measurement period, March 2005 to August 2006.

Figure 3: Diurnal fluxes of CH_3Br measured at the four deciduous woodland enclosures on a day in (a) summer and (b) winter. The pair of arrows on each figure mark the times of local sunrise and sunset. The dashed lines indicate the limit of detection of a net CH_3Br flux.

Figure 4: Net CH_3Br flux measured from two to eight sub-samples of deciduous leaf litter from the Hermitage woodland in Edinburgh during two autumn/winter periods. Data values are mean ± standard error of the sub-samples. The dashed line marks the detection limit for quantifying a net flux in these measurements.

Figure 5: Net CH_3Br flux measured from two to four sub-samples of coniferous needle litter from two conifer woodlands (March-June 2006, Griffin Forest, Perthshire; November 2006-January 2007, Hermitage, Edinburgh). Data values are mean ± standard error of the sub-samples. The dashed line marks the detection limit for quantifying a net flux in these measurements.

Figures

Figure 1:

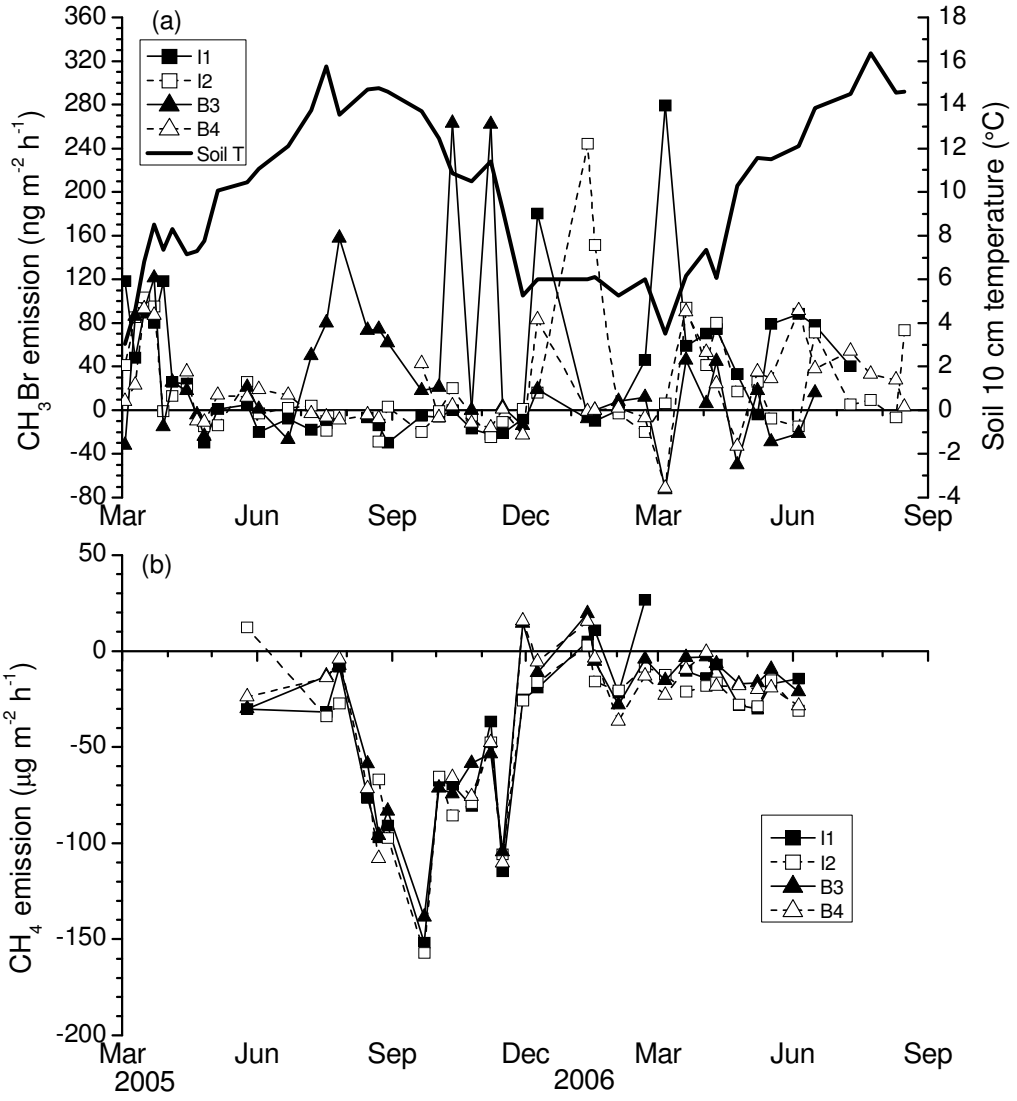

Figure 2:

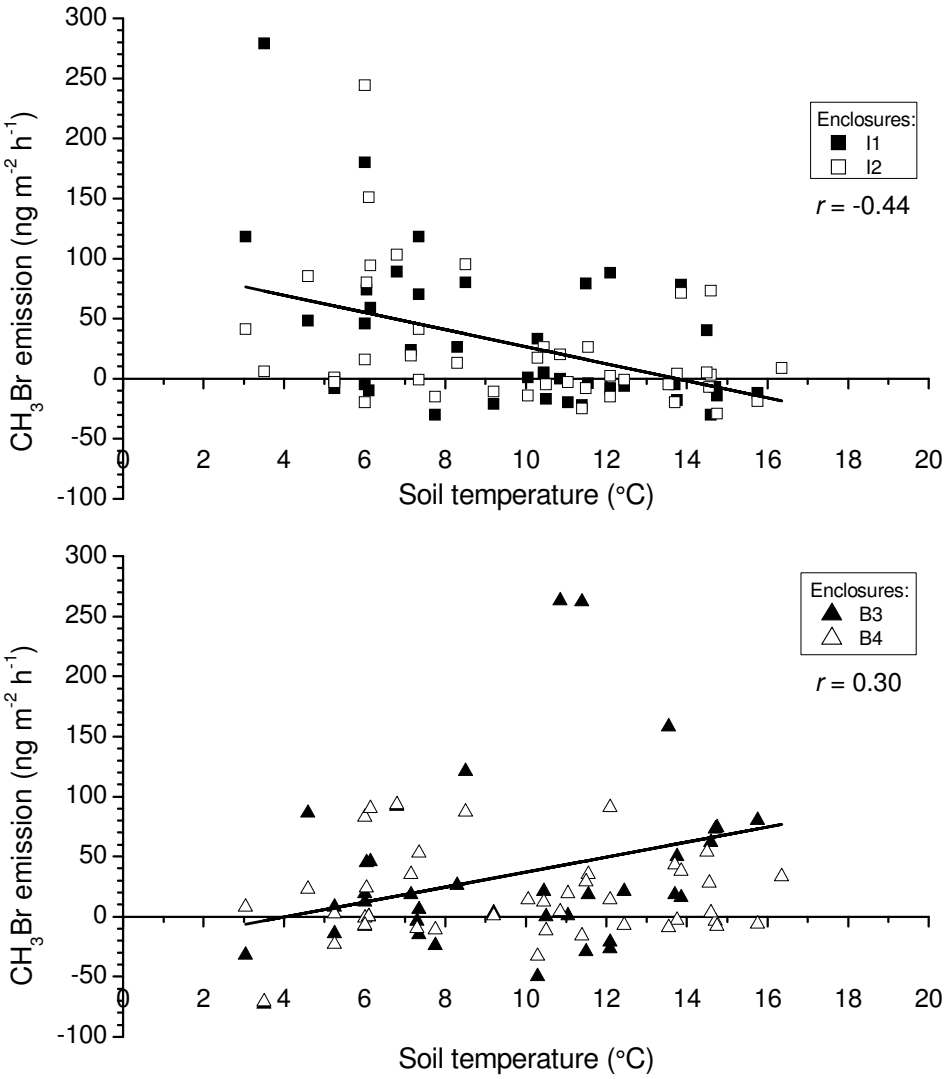
Enclosures:
I1
I2
r = -0.44
CH3Br emission (ng m-2 h-1)
Soil temperature (°C)
Enclosures:
B3
B4
r = 0.30
CH3Br emission (ng m-2 h-1)
Soil temperature (°C)

Figure 3:

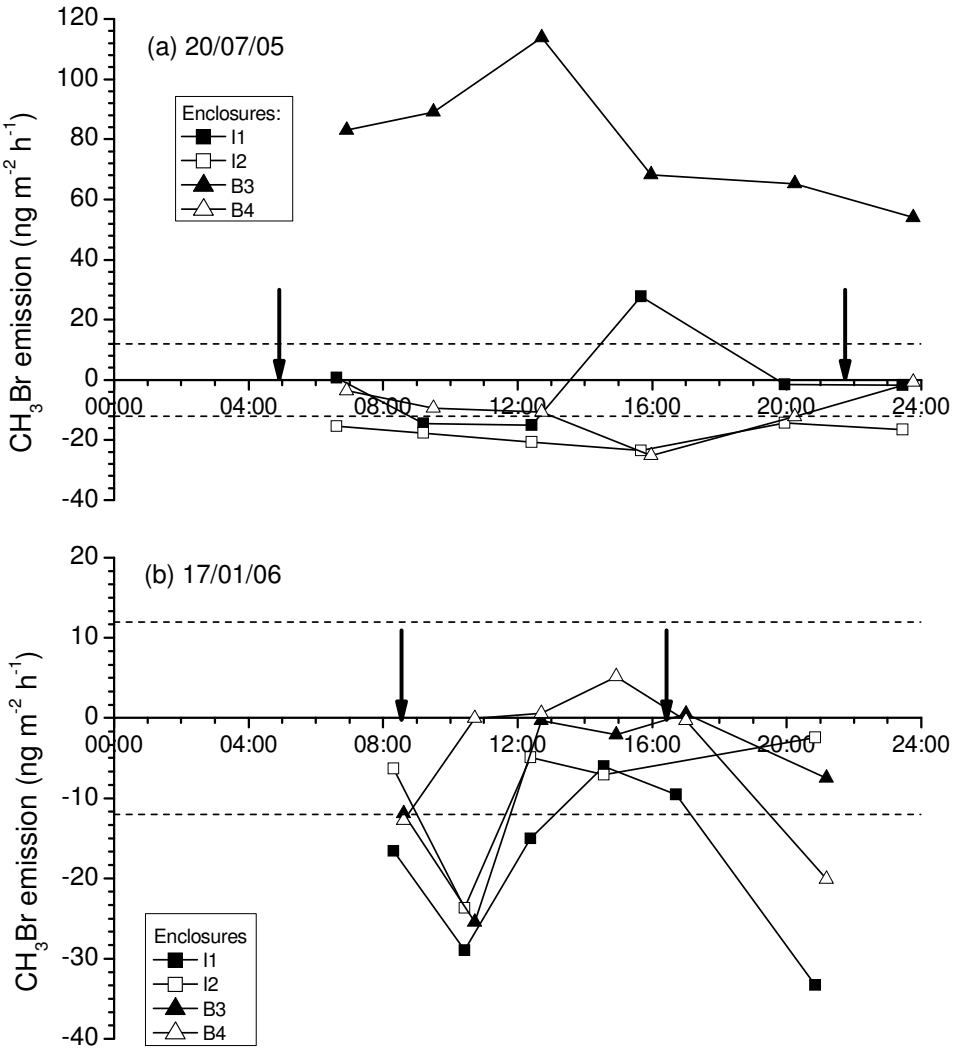
(a) 20/07/05
Enclosures:
I1
I2
B3
B4
CH_3Br emission (ng m^{-2} h^{-1})
120
100
80
60
40
20
0
-20
-40
00:00
04:00
08:00
12:00
16:00
20:00
24:00
(b) 17/01/06
Enclosures
I1
I2
B3
B4
CH_3Br emission (ng m^{-2} h^{-1})
20
10
0
-10
-20
-30
-40
00:00
04:00
08:00
12:00
16:00
20:00
24:00

Figure 4:

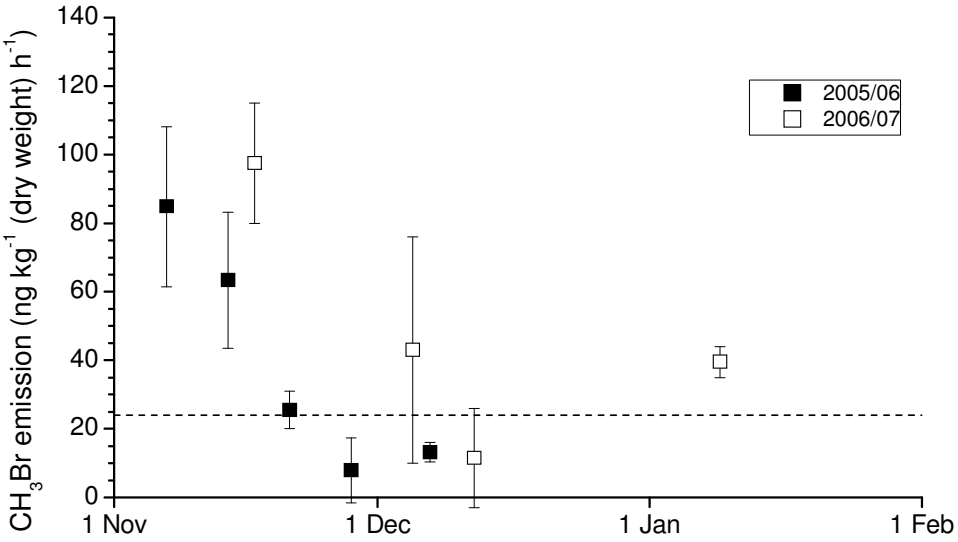

Figure 5: